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Form PTO-1390 (Rev. 12-29-99)		US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NO <b>H 3910 PCT/US</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (if known see 37 CFR 1.5) <b>10/049978</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/07850</b>	INTERNATIONAL FILING DATE <b>August 11, 2000</b>	PRIORITY DATE CLAIMED <b>August 20, 1999</b>	
TITLE OF INVENTION <b>ACCELERATOR FOR PHOSPHATING METAL SURFACES</b>			
APPLICANT(S) FOR DO/EO/US <b>Bernd SCHENZLE, Franz-Adolf CZIKA and Peter KUHM</b>			
Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:			
<ol style="list-style-type: none"><li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li><li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li><li>3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).</li><li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li><li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)).<ol style="list-style-type: none"><li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li><li>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li><li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li></ol></li><li>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li><li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))<ol style="list-style-type: none"><li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li><li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li><li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li><li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li></ol></li><li>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li><li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <b>(UNEXECUTED)</b></li><li>10. <input checked="" type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li></ol>			
Items 11. to 16. below concern other document(s) or information included:			
<ol style="list-style-type: none"><li>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li><li>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li><li>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li><li>14. <input type="checkbox"/> A substitute specification.</li><li>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</li><li>16. <input checked="" type="checkbox"/> Other items or information:  International Search Report (With Information Disclosure Citation and References)</li></ol>			
"Express Mail" mailing label number <u>EL 615775105 US</u>			

U.S. Application No. (If known, see 37 CFR 1.5) <div style="font-size: 1.5em; font-weight: bold;">10/049978</div>	INTERNATIONAL APPLICATION NO. <b>PCT/EP00/07850</b>	ATTORNEY'S DOCKET NUMBER <b>H 3910 PCT/US</b>
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17. The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....**\$1,040.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....**\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37CFR 1.445(a)(2)) paid to USPTO .....**\$740.00**

International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **\$710.00**

International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4).....**\$100.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total Claims	26 - 20 =	6	6 X \$18.00
Independent Claims	3 - 3 =	0	0 X \$84.00
Multiple dependent claims (s)(if applicable)		0	+ \$280.00
<b>TOTAL OF ABOVE CALCULATIONS =</b>			
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).			
<b>SUBTOTAL =</b>			
Processing fee of <b>\$130.00</b> for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			
<b>TOTAL NATIONAL FEE =</b>			
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property			
<b>TOTAL FEES ENCLOSED =</b>			

Amount to be refunded:

charged:

Amount to be: \$-----

charged: \$ 998. 00

SIGNATURE:

Glenn E. J. Murphy

NAME ATTORNEY FOR APPLICANT

33,539

REGISTRATION NUMBER

a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 01-1250 in the amount of \$ 998.00 to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. 02-0088.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-1250. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

Henkel Corporation, Law Dept.  
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Gulph Mills, PA 19406

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PATENT  
Docket H 3910 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Re: PCT/EP00/07850

International Filing Date:	August 11, 2000
Priority Dates:	August 20, 1999
Applicant:	SCHENZLE, et al.
Title:	ACCELERATOR FOR PHOSPHATING METAL SURFACES

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents  
Washington, DC 20231

Please enter the amendments below before examining this  
application on the merits:

IN THE SPECIFICATION:

On page 1, insert below the title:

--CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a U.S. National Stage application  
under 35 U.S.C. § 371 of International Application No.  
PCT/EP00/07850, claiming priority under 35 U.S.C. § 365 of  
PCT/EP00/07850, filed in the European Patent Office August  
11, 2000, and under 35 U.S.C. § 119 of DE 199 39 519.5,  
filed in the German Patent Office August 20, 1999.--

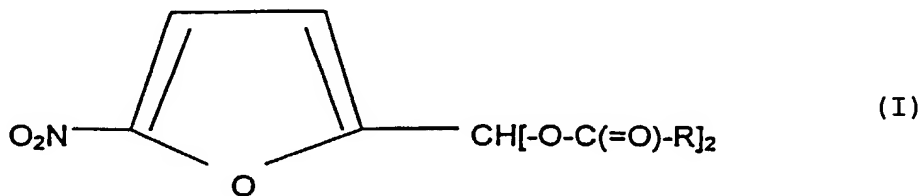
On page 3, after line 11, insert the heading:

--DESCRIPTION OF THE INVENTION--.

IN THE CLAIMS:

Please cancel claims 1-9 without prejudice and enter  
new claims 10-35:

10. An acidic, aqueous phosphating solution comprising from  
0.2 to 3 g/l of zinc ions, from 3 to 50 g/l of phosphate  
ions, calculated as  $\text{PO}_4^{3-}$ , and from 0.5 to 5 g/l of at least  
one organic nitro compound selected from the group consisting  
of nitroarginine, its esters with alcohols having from 1 to 4  
carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates  
corresponding to the general formula (I):



wherein R represents an alkyl group having from 1 to 3  
carbon atoms.

11. The solution of claim 10, comprising from 0.8 to 3 g/l  
of the at least one organic nitro compound.

12. The solution claim 10, further comprising one or more of  
the following cations:

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from 0.1 to 4 g/l of manganese(II);  
from 0.2 to 2.5 g/l of magnesium(II);  
from 0.2 to 2.5 g/l of calcium(II);  
from 0.002 to 0.2 g/l of copper(II); or  
from 0.1 to 2 g/l of cobalt(II).

13. The solution claim 11, further comprising one or more of the following cations:

from 0.1 to 4 g/l of manganese(II);  
from 0.2 to 2.5 g/l of magnesium(II);  
from 0.2 to 2.5 g/l of calcium(II);  
from 0.002 to 0.2 g/l of copper(II); or  
from 0.1 to 2 g/l of cobalt(II).

14. The solution of claim 12, comprising from 0.1 to 4 g/l of manganese ions and from 0.002 to 0.2 g/l of copper ions, and further comprising not more than 0.05 g/l of nickel ions.

15. The solution of claim 12, comprising from 0.1 to 4 g/l of manganese ions, and further comprising from 0.1 to 2.5 g/l of nickel ions.

16. The solution of claim 10, comprising from 0.4 to 2 g/l of zinc ions.

17. The solution of claim 16, comprising from 0.5 to 1.5 g/l of zinc ions.

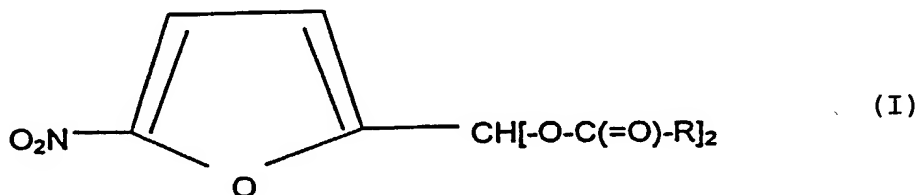
18. The solution of claim 11, comprising from 0.4 to 2 g/l of zinc ions.

19. The solution of claim 18, comprising from 0.5 to 1.5 g/l of zinc ions.

20. The solution of claim 12, comprising from 0.4 to 2 g/l of zinc ions.

21. The solution of claim 20, comprising from 0.5 to 1.5 g/l of zinc ions.

22. An aqueous concentrate comprising from 0.36% to 46.15% by weight of zinc ions, from 27.27% to 95.24% by weight of phosphate ions, and from 0.93% to 60.96% by weight of at least one organic nitro compound selected from the group consisting of nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates corresponding to the general formula (I):



wherein R represents an alkyl group having from 1 to 3 carbon atoms, said weight percents based on the combined weight of zinc ions, phosphate ions, and organic nitro compounds present in the concentrate.

23. The aqueous concentrate of claim 22, further comprising one or more of the following cations:

from 0.17% to 108.11% by weight of manganese(II);  
from 0.34% to 67.57% by weight of magnesium(II);  
from 0.34% to 67.57% by weight of calcium(II);  
from 0.0034% to 5.4% by weight of copper(II); or  
from 0.17% to 54.05% by weight of cobalt(II).

24. The aqueous concentrate of claim 22, comprising 1.50% to 36.59% by weight of the at least one organic nitro compound.

25. The aqueous concentrate of claim 23, comprising from 0.17% to 108.11% by weight of manganese(II) ions and from 0.0034% to 5.4% by weight of copper(II) ions, and further comprising not more than 1.35% by weight of nickel ions.

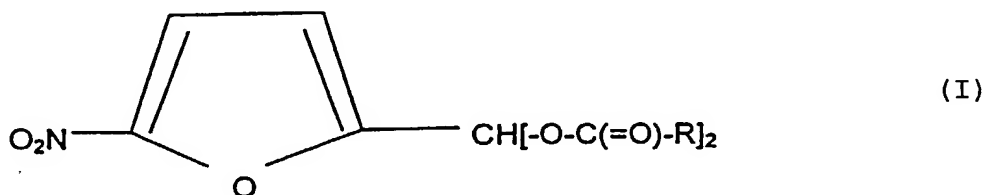
26. The aqueous concentrate of claim 23, comprising from 0.17% to 108.11% by weight of manganese(II) ions, and further comprising 0.17% to 67.57% by weight of nickel ions.

27. The aqueous concentrate of claim 22, comprising from 0.72% to 36.36% by weight of zinc ions.

28. The aqueous concentrate of claim 27, comprising from 0.90% to 30.00% by weight of zinc ions.

29. A process for phosphating metal surfaces of steel, galvanised or alloy-galvanised steel, and aluminum, comprising the steps of contacting such a metal surface by spraying or immersion or a combination thereof, for a period of from 3 seconds to 8 minutes, with an aqueous phosphating solution

comprising from 0.2 to 3 g/l of zinc ions, from 3 to 50 g/l of phosphate ions, calculated as  $\text{PO}_4^{3-}$ , and from 0.5 to 5 g/l of at least one organic nitro compound selected from the group consisting of nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates corresponding to the general formula (I):



wherein R represents an alkyl group having from 1 to 3 carbon atoms.

30. The process of claim 29, wherein the aqueous phosphating solution comprises ~~from~~ 0.8 to 3 g/l of the at least one organic nitro compound.

31. The process of claim 29, wherein the aqueous phosphating solution further comprises one or more of the following cations:

- from 0.1 to 4 g/l of manganese(II);
- from 0.2 to 2.5 g/l of magnesium(II);
- from 0.2 to 2.5 g/l of calcium(II);
- from 0.002 to 0.2 g/l of copper(II); or
- from 0.1 to 2 g/l of cobalt(II).

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32. The process of claim 31, wherein the aqueous phosphating solution comprises from 0.1 to 4 g/l of manganese ions and from 0.002 to 0.2 g/l of copper ions, and further comprises not more than 0.05 g/l of nickel ions.

33. The process of claim 31, wherein the aqueous phosphating solution comprises from 0.1 to 4 g/l of manganese ions, and further comprises from 0.1 to 2.5 g/l of nickel ions.

34. The process of claim 29, wherein the aqueous phosphating solution comprises from 0.4 to 2 g/l of zinc ions.

35. The process of claim 34, wherein the aqueous phosphating solution comprises from 0.5 to 1.5 g/l of zinc ions.

REMARKS

Applicants cancel claims 1-9 without prejudice, and enter new claims 10-35. The subject matter of the new claims is described the specification at page 3, line 13 to page 6, line 4, line 6, as well as in the original claims. Note that the weight percentages in new claims 22-28 correspond to the gram per liter concentrations found in the specification and original claims. The specification now includes a cross-reference to related applications and headings appropriate to U.S. practice. No new matter has been added.

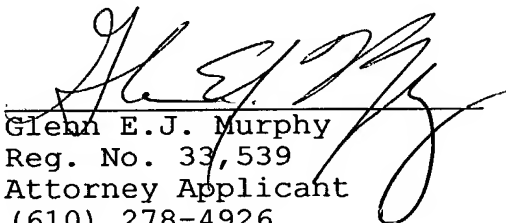
The new claims better claim the full literal and equivalent scope and breadth of subject matter disclosed in the application, notwithstanding applicants' belief that the

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original claims, drafted for examination in the German and European Patent Offices, would have been allowable but for minor matters of form permitted in German or European practice but objected to in the U.S.P.T.O. The new claims find support in the application independent of the original claims and therefore are not believed to constitute narrowing amendments to the original claims within the holding of Festo Corp. v. Shoketsu Kinzoku Kogyo Kabushiki Co., No. 95-1066 (Fed. Cir. Nov. 29, 2000).

Applicants respectfully request entry of this Amendment and examination of the application. If any fees are due to enter this paper that have not been accounted for, please charge Deposit Account No. 01-1250.

Respectfully submitted,

  
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19.08.1999

- 1 -

# **"Accelerator for the phosphating of metal surfaces"**

This invention relates to a phosphating solution, to a phosphating concentrate and to a process for the phosphating of metal surfaces using aqueous, acidic phosphating solutions. The phosphating may be iron phosphating or zinc phosphating. The process is especially zinc phosphating used to pretreat the metal surfaces for subsequent lacquering, especially electro-dipcoating. The process may be used for treating surfaces of steel, galvanised or alloy-galvanised steel, aluminum, aluminised or alloy-aluminised steel.

The aim of the phosphating of metals is to produce metal phosphate layers which are adhered to the metal surface and which by themselves improve corrosion resistance and, in conjunction with lacquers and other organic coatings, contribute towards substantially increasing adhesion and resistance to creepage when subjected to corrosion. Such phosphating processes have long been known in the art. For pretreatment prior to lacquering, the low-zinc phosphating processes in particular, are suitable, in which the phosphating solutions contain comparatively small amounts of zinc ions of, for example, from 0.5 to 2 g/l. An important parameter in those low-zinc phosphating baths is the weight ratio of phosphate ions to zinc ions, which is usually  $> 12$  and may assume values of up to 30.

It has been found that by the concomitant use of polyvalent cations other than zinc in the phosphating baths, it is possible to produce phosphate layers having markedly improved corrosion-protective and lacquer-adhesive properties. For example, low-zinc processes with the addition of, for example, from 0.5 to 1.5 g/l of manganese ions and, for example, from 0.3 to 2.0 g/l of nickel ions are widely used as so-called trication processes for preparing metal surfaces for lacquering, for example for the cathodic electro-dipcoating of motor vehicle bodies.

DE-A-40 13 483 discloses phosphating processes with which it is possible to achieve corrosion-protective properties similar to those achieved with the trication processes.

Those processes do not use nickel and instead employ copper in low concentrations, from 0.001 to 0.03 g/l. For the oxidation of the divalent iron formed in the corrosive reaction of steel surfaces to the trivalent state, oxygen and/or other oxidising agents having an equivalent action are used. There are mentioned as such oxidising agents, nitrite, chlorate, bromate, peroxy compounds and organic nitro compounds, such as nitrobenzenesulfonate. German Patent Application DE 42 10 513 modifies that process by using hydroxylamine as the modifying agent for the morphology of the phosphate crystals that are formed, the hydroxylamine salts or complexes being added in an amount of from 0.5 to 5 g/l of hydroxylamine.

The use of hydroxylamine and/or derivatives thereof to influence the shape of the phosphate crystals is known from a number of Offenlegungsschriften. EP-A-315 059 mentions as a particular effect of the use of hydroxylamine in phosphating baths the fact that, on steel, the phosphate crystals are still formed in a desired columnar or nodal shape even if the zinc concentration in the phosphating bath exceeds the usual range for low-zinc processes.

Hydroxylamine has the great advantage in terms of process technology that it generally does not decompose by itself in the phosphating bath and in phosphating concentrates. Accordingly, it is possible to prepare phosphating bath concentrates and supplementary solutions for phosphating baths that contain the required amounts of accelerator directly. The expensive, separate subsequent metering in of the accelerator, as is required, for example, when nitrite or hydrogen peroxide is used as the accelerator, is thus not necessary. However, if the phosphating solution contains copper ions, to which there is a technical trend at present, hydroxylamine gradually decomposes under the catalytic effect of those ions. In that case, the accelerator must be added to the phosphating bath separately and in increased amounts. There is, therefore, a need for new accelerators which may be incorporated, like hydroxylamine, into phosphating baths, concentrates and supplementary solutions thereof, without decomposing in a short time. They must still have this property even if copper ions are present.

From DE-A-197 33 978 there are known zinc phosphating processes in which organic N-oxides, especially cyclic N-oxides, are used as accelerator. A preferred example is N-methylmorpholine N-oxide. Zinc phosphating solutions in which nitroguanidine is used as accelerator are known from DE-A-196 34 685. Hitherto, none of those alternatives to hydroxylamine has been successful in practice.

An object of the present invention is to make available further phosphating processes which have the advantages of hydroxylamine-accelerated processes, but do not have the disadvantages thereof as regards decomposition in the presence of copper ions. It is to be possible to use the phosphating process in the spraying, spraying-immersion or immersion process.

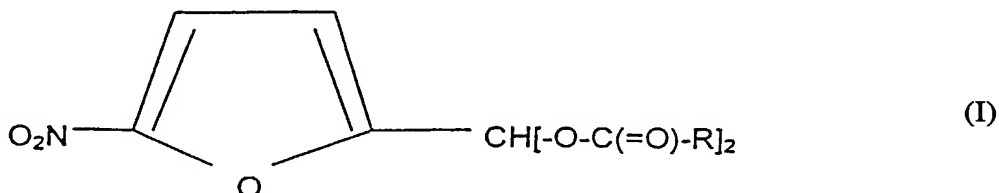
Accordingly, the present invention relates to an acidic, aqueous phosphating solution containing:

from 0.2 to 3 g/l of zinc ions,

from 3 to 50 g/l of phosphate ions, calculated as  $\text{PO}_4^{3-}$ , and

from 0.5 to 5 g/l of at least one organic nitro compound as accelerator,

wherein the organic nitro compound is selected from nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates corresponding to the general formula (I):



wherein R represents an alkyl group having from 1 to 3 carbon atoms.

Nitroarginine may be represented by the chemical formula (II):



Like all amino acids, that compound too is amphoteric, that is to say it is able to form salts with both acids and bases. In the acidic phosphating solution, it is to be expected that the compound is present in cationic form. That is irrespective of whether the compound was used as such, in the form of a salt with a base, for example in the form of an alkali metal salt, or in the form of a salt with an acid, for example in the form of a hydrochloride.

Instead of the amino acid nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms may also be used. Preferred esters are especially methyl esters and ethyl esters. Since the acid function is blocked by the ester formation, the esters cannot be present in the form of salts with a base. However, salt formation with acids is still possible owing to the amino groups. Therefore, the esters too will for the most part, be present in the acidic phosphating solution in the form of cations. They may be introduced into the phosphating solution in the form of a neutral compound, but also already in salt form. For example, hydrochlorides may be used.

If the organic nitro compound is selected from 5-nitro-2-furfuryl dicarboxylates (I), then the diacetate is especially preferred. That means that R in the general formula (I) preferably represents a methyl group.

The phosphating solution preferably contains from 0.8 to 3 g/l of the organic nitro compound.

In addition to zinc ions, phosphating baths generally contain sodium ions, potassium ions and/or ammonium ions for adjusting the free acid. The expression free acid is known to the person skilled in the field of phosphating. The chosen method of determining the free acid and the total acid herein is indicated in the Examples. Free acid values of from 0 to 1.5 points and total acid values of from about 15 to about 35 points are within the technically usual range and are suitable within the scope of the present invention.

The zinc contents are preferably from 0.4 to 2 g/l and especially from 0.5 to 1.5 g/l,

as are customary for low-zinc processes. The weight ratio of phosphate ions to zinc ions in the phosphating baths may vary within wide limits, provided it is within the range of from 3.7 to 30. A weight ratio of from 10 to 20 is especially preferred.

5 There are preferably used in the phosphating process according to the present invention phosphating solutions that contain further mono- or di-valent metal ions which, according to experience, have an advantageous effect on the lacquer adhesion and the corrosion protection of the phosphate layers produced thereby. Accordingly, the phosphating solution according to the present invention preferably additionally  
10 contains one or more of the following cations:

from 0.1 to 4 g/l of manganese(II),  
from 0.2 to 2.5 g/l of magnesium(II),  
from 0.2 to 2.5 g/l of calcium(II),  
15 from 0.002 to 0.2 g/l of copper(II),  
from 0.1 to 2 g/l of cobalt(II).

If desired, the phosphating solutions may additionally contain nickel ions. However, for health and ecological reasons, preference is given to phosphating baths that  
20 contain as small an amount of nickel ions as possible or, if desired, may also be nickel-free. For example, in a preferred embodiment, the phosphating solution according to the present invention contains as additional cations, in addition to zinc ions, from 0.1 to 4 g/l of manganese ions and from 0.002 to 0.2 g/l of copper ions and not more than 0.05 g/l, especially not more than 0.001 g/l, of nickel ions.  
25 However, if it is desired to adhere to conventional trication technology, it is possible to use phosphating baths according to the present invention that contain, in addition to zinc ions, from 0.1 to 4 g/l of manganese ions and, additionally, from 0.1 to 2.5 g/l of nickel ions. The form in which the cations are introduced into the phosphating baths is in principle of no importance. It is possible especially to use oxides and/or  
30 carbonates as the cation source.

In the phosphating of zinc-containing surfaces it has proved advantageous to limit the

nitrate content of the phosphating bath to a maximum of 0.5 g/l. As a result, the problem of so-called "pinholing" is overcome and the corrosion protection is improved, especially where nickel-free phosphating baths are used. Phosphating baths that do not contain nitrate are especially preferred.

5

In the case of phosphating baths that are to be suitable for various substrates, it has become customary to add free and/or coordinated fluoride in amounts of up to 2.5 g/l of total fluoride, of which up to 750 mg/l is free fluoride, in each case calculated as F<sup>-</sup>. The presence of such amounts of fluoride is advantageous also for the phosphating baths according to the present invention. In the absence of fluoride, the aluminum content of the bath should not exceed 3 mg/l. In the presence of fluoride, higher Al contents are tolerated on account of complex formation, provided the concentration of non-complexed Al does not exceed 3 mg/l.

15 In principle, phosphating baths may be prepared directly in situ by dissolving the individual components in water in the desired concentration range. In practice, however, it is usual to use concentrates that contain the individual constituents in the desired relative proportions and from which the ready-for-use phosphating bath is prepared in situ by dilution with water, or that are added to a working phosphating bath as a supplementary solution in order to compensate for depletion of the active components. However, such phosphating concentrates are rendered strongly acidic for the purpose of stabilisation. After dilution with water, therefore, the pH and/or the free acid must often be neutralised to the desired range. To that end, substances having an alkaline action, such as sodium hydroxide solution or sodium carbonate or basic salts or hydroxides of Ca, Mg, Zn, are added.

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Accordingly, the present invention relates also to an aqueous concentrate which, after dilution with water by a factor of from 10 to 100 and, optionally, adjustment of the pH to a working range of from 2.5 to 3.6, gives a phosphating solution according to the present invention.

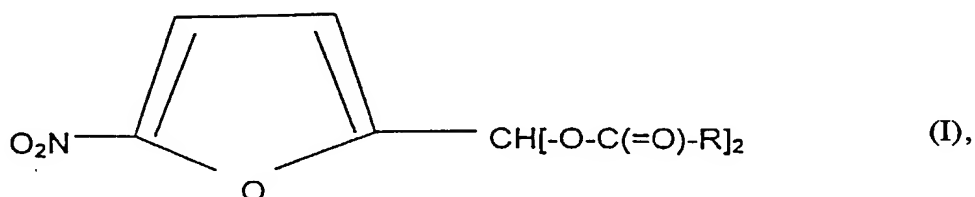
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The present invention also includes a process for the phosphating of metal surfaces

of steel, galvanised or alloy-galvanised steel and/or of aluminum. The mentioned materials may also be present together, as is increasingly common in motor vehicle construction. The metal surfaces are contacted with the phosphating solution according to the present invention by spraying or immersion or by a combination thereof. The temperature of the phosphating solution is preferably from about 40 to about 60°C.

The phosphating process may be used for the phosphating of strips of steel or galvanised steel in strip installations. The phosphating times in that case are from about 3 to about 20 seconds. However, the process may be used especially in motor vehicle construction, where treatment times of from 1 to 8 minutes are usual. It is intended especially for the treatment of the mentioned metal surfaces before lacquering, especially before cathodic electro-dipcoating. The phosphating process is to be regarded as a subsidiary step of the technically usual pretreatment chain. In that chain, the phosphating is generally preceded by the steps cleaning/degreasing, intermediate washing and activation, activation usually being carried out using titanium-phosphate-containing activating agents. The phosphating according to the present invention may be followed, optionally after intermediate washing, by a passivating after-treatment. Chromic acid-containing treatment baths are widely used for such a passivating after-treatment. For reasons of industrial safety and environmental protection and for reasons of disposal, however, there is a tendency to replace those chromium-containing passivating baths by chromium-free treatment baths. There are known for that purpose purely inorganic baths, especially based on zirconium compounds, or organic baths, for example based on poly(vinylphenols). When phosphating solutions containing neither nickel ions nor copper ions are used, a marked improvement in corrosion protection may be achieved if copper ions or silver ions are added to the baths for passivating after-treatment. For example, there may be used passivating after-washing solutions that contain from 0.001 to 10 g/l of copper ions and that may, if desired, be free of other components having a passivating action. Between the after-passivation and the electro-dipcoating which usually follows, intermediate washing with demineralised water is generally carried out.

The organic nitro compounds to be used as accelerator according to the present invention have a positive effect on the formation of the corrosion-protective layer not only in the case of layer-forming zinc phosphating, but also in the case of iron phosphating, which is described as "non-layer-forming". Accordingly, the present invention relates in a generalised aspect to the use of organic nitro compounds selected from nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates corresponding to the general formula (I):



15 wherein R represents an alkyl group having from 1 to 3 carbon atoms, as accelerators in phosphating solutions.

As regards the compounds which are preferably to be used and the possibility that those compounds may also be present in salt form, the comments made above with reference to the example of the zinc phosphating solution apply.

20 The novel phosphating accelerators according to the present invention have the advantage, as compared with hydroxylamine, that they do not undergo catalytic decomposition in the presence of copper. As a result, the amount of accelerator used in copper-containing phosphating baths is reduced as compared with the standard hydroxylamine. Compared with nitroguanidine as the chemically most similar alternative, nitroarginine and its esters are safer to handle: nitroguanidine decomposes at 102°C explosively, nitroarginine does not decompose until 195°C. Nitroarginine methyl ester hydrochloride especially is readily soluble in the acid range (pH about 3.3) and may therefore be used as an internal accelerator.

### Examples

The phosphating processes according to the present invention and comparison processes were tested on St 1405 steel sheets (CRS), electrolytically galvanised steel (EG) and hot-dip galvanised steel (HDG), as are used in motor vehicle construction. In the tests, the following procedure, which is usual in motor vehicle body manufacture, was carried out as the immersion process:

1. Cleaning using an alkaline cleaner (Ridoline<sup>R</sup> 1559, Henkel KGaA), 3% preparation in tap water, 60°C, from 5 to 10 minutes.
2. Washing with tap water, room temperature, 1 minute.
3. Activation using a titanium-phosphate-containing activating agent (FixodineR C 9112, Henkel KGaA), 0.2% preparation in demineralised water, room temperature, 1 minute.
4. Phosphating using phosphating baths according to Table 1  
Total acid: 23 points  
Temperature: 52°C; treatment time: 3 minutes' immersion.

The free acid point value is to be understood as meaning the amount in ml of 0.1N sodium hydroxide solution used to titrate 10 ml of bath solution to a pH of 3.6. By analogy, the total acid point value indicates the amount in ml used to attain a pH of 8.2.

5. Washing with demineralised water, room temperature, 1 minute.
6. Blowing dry using compressed air.
7. Cathodic electro-dipcoating using the lead-free cathodic electro-dipcoating Cathogurad<sup>R</sup> 400 from BASF.

Table 1: Phosphating parameters. Bath concentrations in g/l, free acid: point value

Accelerator: comparison: HAS = hydroxylammonium sulfate, NG = nitroguanidine; according to the present invention: NA = nitro-L-arginine, NE = nitro-L-arginine methyl ester hydrochloride, NF = nitrofurfurylidene diacetate

Component	Comp.1	Ex.1	Ex.2	Comp.2	Comp.3	Ex.3	Ex.4	Comp.5	Comp.6	Ex.5	Ex.6	Ex.7
Zn (II)	1.2	1.2	1.2	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Mn (II)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Ni (II)	0.8	0.8	0.8									
Cu (II)								0.005	0.005	0.005	0.005	0.005
PO <sub>4</sub> <sup>3-</sup>	13.7	13.7	13.7	13.8	13.8	13.8	13.8	13.8	13.8	13.8	13.8	13.8
SiF <sub>6</sub> <sup>2-</sup>	0.9	0.9	0.9	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
NG	2.0				2.0				2.0			
NA		2.0				2.0				2.0		
NE			2.0				2.0				2.0	
NF												1.0
HAS				2.0				2.0				
free acid	0.9	0.9	0.9	1.2	1.2	0.8	0.8	1.2	1.2	0.8	0.8	1.0

11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

An alternating atmosphere test VDA 621415 over 10 rounds and a stone impact test VDA 621427 were carried out as corrosion tests. The results are shown in Table 2. The creepage at the scribe (half scribe width) in mm and, for the stone impact test, the K value (best value = 1, poorest value = 10) are given.

5

Table 2: Results of the corrosion tests: C = creepage (half scribe width, mm), K value

	Phosphating bath	Substrate	C	K value
10	Comp. 1	CRS	1.6	3
	Ex. 1	CRS	1.3	3
15	Ex. 2	CRS	1.2	3
	Comp. 2	CRS	1.5	4
	Comp. 3	CRS	1.5	4
20	Ex. 3	CRS	1.7	3-4
	Ex. 4	CRS	1.7	4
25	Comp. 5	CRS	1.0	3
	Comp. 6	CRS	1.3	3
	Ex. 5	CRS	1.2	3-4
30	Ex. 5	EG	3.8	4
	Ex. 5	HDG	3.5	3-4
35	Ex. 6	CRS	1.3	3-4
	Ex. 6	EG	3.9	4
	Ex. 6	HDG	4.2	3-4
40	Ex. 7	CRS	1.5	3-4
	Ex. 7	EG	3.4	4
45	Ex. 7	HDG	3.7	3-4

**Claims:**

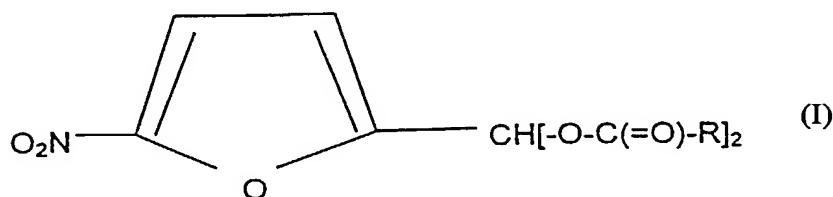
1. An acidic, aqueous phosphating solution containing:

from 0.2 to 3 g/l of zinc ions,

from 3 to 50 g/l of phosphate ions, calculated as  $\text{PO}_4^{3-}$ , and

from 0.5 to 5 g/l of at least one organic nitro compound as accelerator,

characterised in that the organic nitro compound is selected from nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates corresponding to the general formula (I):



wherein R represents an alkyl group having from 1 to 3 carbon atoms.

2. A phosphating solution as claimed in claim 1 wherein it contains from 0.8 to 3 g/l of the organic nitro compound.

3. A phosphating solution as claimed in one or both of claims 1 and 2 wherein it additionally contains one or more of the following cations:

from 0.1 to 4 g/l of manganese(II),

from 0.2 to 2.5 g/l of magnesium(II),

from 0.2 to 2.5 g/l of calcium(II),

from 0.002 to 0.2 g/l of copper(II),

from 0.1 to 2 g/l of cobalt(II).

4. A phosphating solution as claimed in claim 3 wherein it contains from 0.1 to 4 g/l of manganese ions and from 0.002 to 0.2 g/l of copper ions and not more than 0.05 g/l of nickel ions.

5 5. A phosphating solution as claimed in claim 3 wherein it contains from 0.1 to 4 g/l of manganese ions and additionally from 0.1 to 2.5 g/l of nickel ions.

6. A phosphating solution as claimed in one or more of claims 1 to 5 wherein it contains from 0.4 to 2 g/l, preferably from 0.5 to 1.5 g/l, of zinc ions.

10

7. An aqueous concentrate which, after dilution with water by a factor of from 10 to 100 and, optionally, adjustment of the pH to a working range of from 2.5 to 3.6, gives a phosphating solution as claimed in one or more of claims 1 to 6.

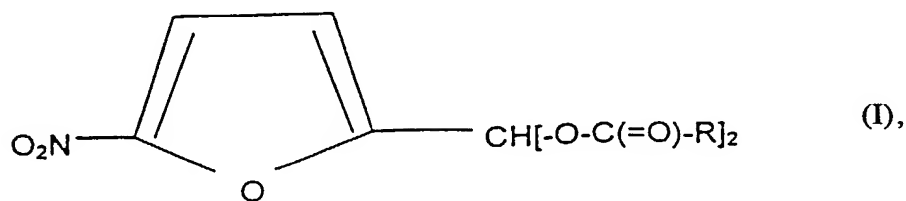
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8. A process for the phosphating of metal surfaces of steel, galvanised or alloy-galvanised steel and/or of aluminum, in which the metal surfaces are contacted by spraying or immersion, or by a combination thereof, for a period of from 3 seconds to 8 minutes with a phosphating solution as claimed in one or more of claims 1 to 6.

20

9. Use of organic nitro compounds selected from nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates corresponding to the general formula (I):

25



30

wherein R represents an alkyl group having from 1 to 3 carbon atoms, as accelerators in phosphating solutions.

- 14 -

**Abstract**

**"Accelerator for the phosphating of metal surfaces"**

An acidic, aqueous phosphating solution containing:

- 5 from 0.2 to 3 g/l of zinc ions,
  - from 3 to 50 g/l of phosphate ions, calculated as  $\text{PO}_4^{3-}$ , and
  - from 0.5 to 5 g/l of at least one organic nitro compound as accelerator,
- wherein the organic nitro compound is selected from nitroarginine, its esters with alcohols having from 1 to 4 carbon atoms, and 5-nitro-2-furfurylidene dicarboxylates.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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(84) Bestimmungsstaaten (regional): europäisches Patent (AT,  
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NL, PT, SE).

Veröffentlicht:

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Zur Erklärung der Zweibuchstaben-Codes und der anderen  
Abkürzungen wird auf die Erklärungen ("Guidance Notes on  
Codes and Abbreviations") am Anfang jeder regulären Ausgabe  
der PCT-Gazette verwiesen.

(54) Title: ACCELERATOR FOR PHOSPHATING METAL SURFACES

(54) Bezeichnung: BESCHLEUNIGER FÜR DIE PHOSPHATIERUNG VON METALLOBERFLÄCHEN

(57) Abstract: The invention relates to an acidic, aqueous phosphating solution that contains 0.2 to 3 g/l zinc ions, 3 to 50 g/l phosphate ions, calculated as  $\text{PO}_4^{3-}$  and 0.5 to 5 g/l of at least one organic nitro compound as the accelerator. The inventive compound is further characterized in that the organic nitro compound is selected from nitroarginine, its esters with alcohols with 1 to 4 C atoms and 5-nitro-2-furfurylidene dicarboxylates.

(57) Zusammenfassung: Saure, wäßrige Phosphatierlösung, enthaltend 0,2 bis 3 g/l Zinkionen, 3 bis 50 g/l Phosphationen, berechnet als  $\text{PO}_4^{3-}$  und 0,5 bis 5 g/l mindestens eine organische Nitroverbindung als Beschleuniger, dadurch gekennzeichnet, daß die organische Nitroverbindung ausgewählt ist aus Nitroarginin, dessen Estern mit Alkoholen mit 1 bis 4 C-Atomen und aus 5-Nitro-2-furfurylidendicarboxylaten.

WO 01/14613 A3



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## DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket  
Number

H 3910 PCT/US

First Named  
Inventor

SCHENZLE, Bernd

### COMPLETE IF KNOWN

Application Number

10/049,978

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that

My residence, post office address, and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**ACCELERATOR FOR PHOSPHATING METAL SURFACES**

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY)

8/11/2000

as United States Application Number or PCT International

Application Number PCT/EP00/07850

and was amended on (MM/DD/YYYY)

(if applicable)

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Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority		Certified Copy Attached?	
			Not Claimed		YES	NO
199 39 519.5	Germany	8/20/1999	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
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U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP00/07850	8/11/2000	

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As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith

☐ Firm Name  Customer Number  or label

☒ List Attorney(s) and/or agent(s) name and registration number below

Name	Registration Number	Name	Registration Number
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Stephen D. Harper	33,243		
Kimberly R. Hild	39,224		
Steven C. Bauman	33,832		

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Address	Henkel Corporation				
Address	2500 Renaissance Blvd, Suite 200				
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Country	USA	Telephone	610-278-4926	Fax	610-278-6548

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

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Post Office Address	2450 John R. Road 206						
Post Office Address							
City	Troy	State	MI	Zip	48083	Country	US
Applicant Authority							

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

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<b>DECLARATION</b>					<b>ADDITIONAL INVENTOR(S) Supplemental Sheet</b>				
<b>Name of Additional Joint Inventor, if any:</b>					<input type="checkbox"/> A petition has been filed for this unsigned inventor				
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Inventor's Signature						Date			
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City	<b>41470 Neuss</b>	State		Zip		Country	<b>Germany</b>	Applicant Authority	
<b>Name of Additional Joint Inventor, if any:</b>					<input type="checkbox"/> A petition has been filed for this unsigned inventor				
Given Name	<b>Peter</b>	Middle Initial		Family Name	<b>KUHM</b>	Suffix e.g. Jr			
Inventor's Signature						Date			
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Inventor's Signature						Date			
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Inventor's Signature						Date			
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<b>DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION</b>  <input type="checkbox"/> Declaration Submitted with Initial Filing    OR <input checked="" type="checkbox"/> Declaration Submitted after Initial Filing	0010/PTO Rev. 6/95	U.S. Department of Commerce Patent and Trademark Office	Attorney Docket Number	H 3910 PCT/US
			First Named Inventor	SCHENZLE, Bernd
	COMPLETE IF KNOWN			
			Application Number	10/049,978
			Filing Date	
			Group Art Unit	
			Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

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(Title of the Invention)

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	PCT/EP00/07850	8/11/2000	

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As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

<input type="checkbox"/> Firm Name OR		Customer Number	or label	
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☒ List Attorney(s) and/or agent(s) name and registration number below:

Name	Registration Number	Name	Registration Number
Glenn E. J. Murphy	33,539		
Stephen D. Harper	33,243		
Kimberly R. Hild	39,224		
Steven C. Bauman	33,832		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Please direct all correspondence to: ☒ Customer Number or label 00423 OR ☒ Fill in correspondence address below

Name	Glenn E. J. Murphy						
Address	Henkel Corporation						
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor					
Given Name	Bernd	Middle Initial		Family Name	SCHENZLE	Suffix e.g. Jr.	
Inventor's Signature						Date	
Residence: City	Troy	State	MI	Country	US	Citizenship	Germany
Post Office Address	2450 John R. Road 206						
Post Office Address							
City	Troy	State	MI	Zip	48083	Country	US
						Applicant Authority	
<input checked="" type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto							

(+) inside this box → ☐

H 3910 PCT/US

DECLARATION					ADDITIONAL INVENTOR(S) Supplemental Sheet		
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Franz-Adolf	Middle Initial		Family Name	CZIKA	Suffix e.g. Jr.	
Inventor's Signature	Franz-Adolf Czika				Date	15. 02. 2002	
Residence: City	Neuss	State		Country	Germany	Citizenship	Germany
Post Office Address	Fehrenstr. 24						
Post Office Address							
City	41470 Neuss	State		Zip		Country	Germany
						Applicant Authority	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Peter	Middle Initial		Family Name	KUHM	Suffix e.g. Jr.	
Inventor's Signature	Peter Kuhn				Date	15. 02. 2002	
Residence: City	Hilden	State		Country	Germany	Citizenship	Germany
Post Office Address	Clarenbachweg 3						
Post Office Address							
City	40724 Hilden	State		Zip		Country	Germany
						Applicant Authority	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
						Applicant Authority	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
						Applicant Authority	
<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto							